Ultrananocrystalline Diamond: Tuning Materials Properties via Plasma Chemistry

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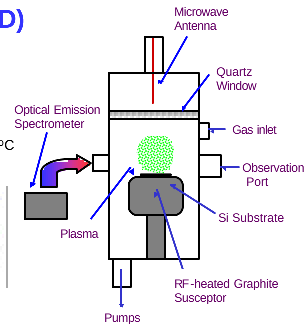
ABSTRACT

Ultra-nanocrystalline diamond (UNCD) films are synthesized by a microwave plasma enhanced chemical vapor deposition (MPCVD) method using a CH_4 (1%)/Ar (99%) gas mixture. Tuning the electrical and structural characteristics of the films is performed via substituting a percentage of the Ar with 1-20% N or H. Electron microscopies indicate a change in grain size and shape, and x-ray spectroscopies indicate local changes in bonding structure. Most strikingly, the electrical conductivity of the nitrogen-doped UNCD films increases by five orders of magnitude (up to 143 Ω^{-1}cm^{-1}) with increasing nitrogen content. Conductivity and Hall measurements indicate that these films have the highest n-type conductivity and carrier concentration demonstrated for phase-pure diamond thin films. Grain boundary conduction is proposed to explain the remarkable transport properties of these films.

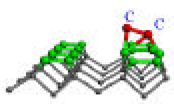
Ultrananocrystalline Diamond (UNCD)

Synthesis:
Microwave Plasma Chemical Vapor Deposition



__Deposition Parameters__:
Plasma Composition: Ar/CH_4 99%/1% Total Pressure: 100 Torr, T_{sub}=800°C

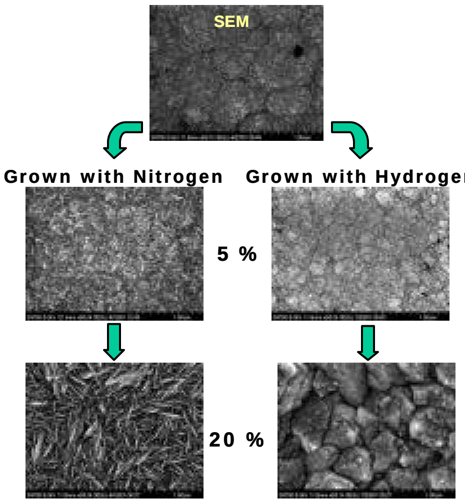
__Growth Mechanism__: C_2 dimer insertion



__Structural Properties:__
- 2-5 nm grain sizes; atomically-abrupt grain boundaries; conformal coating
- Phase-pure (<3% sp^2-bonded carbon)

Control of Structural Properties in UNCD

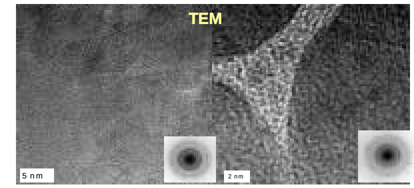
Surface Morphology of Plain UNCD



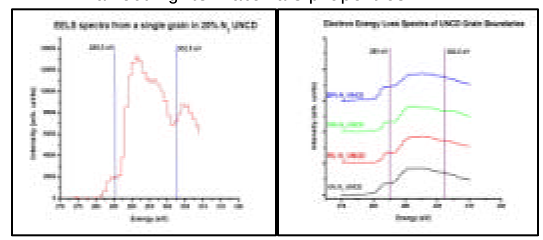
- The bulk structure & surface morphology can be controlled by altering the growth plasma chemistry

Nitrogen Growth: UNCD Structure

Ar:99 / CH_4:1 Ar:79 / CH_4:1 / N_2:20



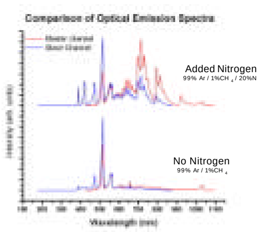
- Nitrogen doping of UNCD alters the nanostructure of the film, in turn affecting its materials properties.

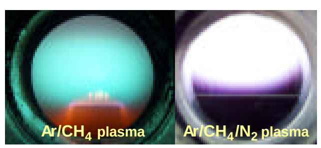


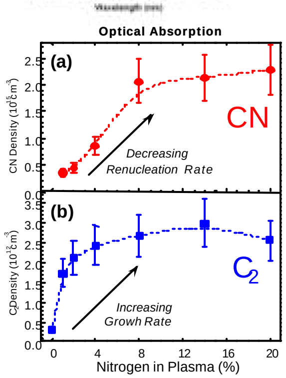
- UNCD grains = phase pure diamond
- UNCD grain boundaries = disordered C

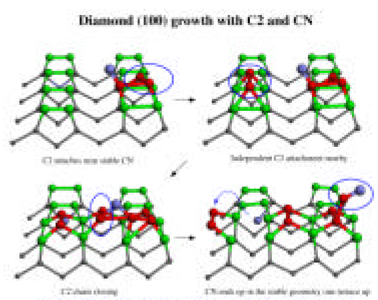
Control of Plasma Growth Species with Nitrogen

- Addition of N (1-20%) increases C_2 dimer and CN specie concentrations



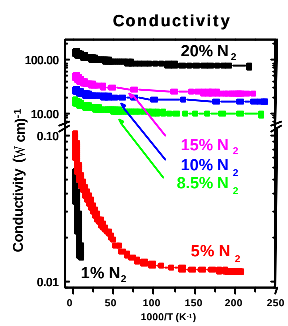




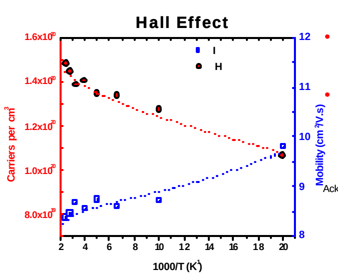


- CN and C_2 co-adsorption leads to CN-mediated C_2 chain growth.
- CN addition does not lead to nucleation; C_2 addition results in both growth and nucleation

Control of Electronic Properties



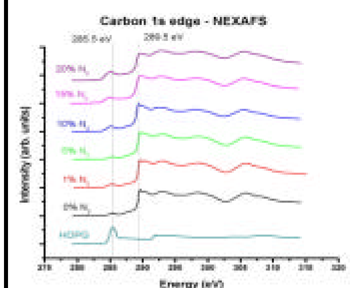
- N doping: UNCD becomes semi-metallic with grain boundaryconductivity
- H doping: UNCD becomes insulating
- The conductivity is a strong fcn. of % N in plasma.
- Results similar to heavily boron-doped diamond



- UNCD is an n-type semiconductor
- %N in plasma tunes carrier concentration and mobility.

Acknowledgment: Lake Shore Cryotronics for Hall Measurements.

Control of Structural Composition



- Moderate increase of sp^2/ sp^3 bonded C ratio
- TEM indicates pure diamond structure in grains
- May indicate grain boundary character is changing

Acknowledgement: Advanced Light Source, Lawrence Berkeley National Laboratory

Summary/Future work

In summary, control over structural and electronic UNCD properties has been demonstrated via N and H doping. Doping with N has in particular proven to be useful for producing highly-conductive, n-type UNCD. We propose that grain boundary conduction involving carbon π-states is responsible for the high electrical conductivities in these films.

Near-future work will include increasing the electronic capabilities of UNCD via doping with B and P and fabricating initial electronic devices, simultaneously controlling the film structure with N or H.

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